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AN INVESTIGATION INTO THE ADHESION OF POLYURETHANE COATINGS USING MATHEMATICAL STATISTICAL METHODS

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AN INVESTIGATION INTO THE ADHESION OF POLYURETHANE COATINGS USING MATHEMATICAL STATISTICAL METHODS

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The adhesion properties of polyurethane coatings (Pc) are affected by the density of the spacial network (given by the original ratio of the isocyanate and glycol components Q), the amount of filler N and the temperature at which the Pc is used [1-3]. It is also known that an increase in the rate of the breakdown stress (rate of shear V) [4] leads to an increase in the limit of resistance to breakdown, while a change in the temperature of the test T affects this quantity in different ways.

For finding a mathematical model which expresses the relationship between the adhesion A and the factors enumerated, mathematical statistical methods were used, with planning of the experiment [5, p. 501; 6, p. 30; 7, pp. 8-137].

For the investigations we used polyurethane obtained from an oligomer of [illegible] tetramethylene) glycol with 25% oxypropylene chains of mol. wt. 1280 and [illegible] trimethylol propane with toluylenediisocyanate, a trifunctional linking agent. The compositions were prepared as 60% solutions in cyclohexane, with excess of isocyanate groups 1.1; 2.1 and 3.1 in relationship to the hydroxyls. The filler was TiO_2, rutile form, in amounts shown in the table.

Limits for change of variables in studying adhesion of polyurethane

Factors	X_1 (N %)	X_2 (v cm/S)	X_3 (T °C)
Basic level 0	30	0.1	40
Upper level + 1	45	0.15	55
Lower level - 1	15	0.05	25
Range of change	15	0.05	15

The investigation of A was carried out on a roller adhesiometer [8, 11]. The compositions obtained were put on steel test rollers, which had been precleaned using the method described in [3].

In order to express A as a function of the factors studied, for a given ratio of NCO/OH, a plan was used which permitted the finding of an equation of the second order (plan B_3). The previously selected area of study and the limits for the variables which presented the greatest interest from the practical viewpoint are shown in the table. After finding the experimental values of A for each NCO/OH ratio these were used to calculate a regression equation. It should be noted that an attempt to use plan B_4, in which the molar ratios of NCO/OH were included as an independent variable, led to the obtaining of an inadequate regression equation. This is evidence of the complicated nature of the surface of response of the process studied, from independent parameters. Because of this, we went over to the description of the value A as a function of independent variables individually,

for each of the relationships obtained. On the basis of the experimental data (not given because of lack of space) we obtained equations for the regression having the form:

$$A_1 = 10.35 + 5.87\chi_1 + 2.19\chi_2 - 2.69\chi_3 + 0.85\chi_1\chi_2 - $$
$$- 1.50\chi_1\chi_3 + 1.90\chi_1^2 - 0.24\chi_2^2 - 0.07\chi_3^2 \quad (1)$$

$$A_2 = 35.48 - 1.79\chi_1 + 2.01\chi_2 - 6.23\chi_3 - 0.34\chi_1\chi_3 -$$
$$- 4.39\chi_1^2 - 0.56\chi_2^2 - 1.53\chi_3^2 \quad (2)$$

$$A_3 = 22.95 + 4.51\chi_1 + 2.12\chi_2 - 5.99\chi_3 - 0.38\chi_1^2 -$$
$$- 0.74\chi_2^2 - 0.46\chi_3^2 \quad (3)$$

$$\chi_1 = \frac{N - 30}{15}, \qquad \chi_2 = \frac{v - 0.1}{0.05}, \qquad \chi_3 = \frac{T - 40}{15},$$

A_1, A_2, and A_3 are the adhesive work of the compositions respectively for NCO/OH ratios of 1.1/1, 2.1/1 and 3.1/1.

The significance of the coefficients in the equations given was determined using the "student" criterion. Insignificant coefficients were discarded. A test on the adequacy (correspondance of the mathematical models found with the experimental data) was made using the Fischer criterion [6]. The calculated values of the F criterion were significantly lower than those in the table, which shows their adequacy.

The regression equations obtained make it possible to evaluate the proportion of contribution of each of the independent variables, with their simultaneous effect on the common magnitude A. On the basis of analysis of the coefficients of the equations it is possible to come to the conclusion that the effect of v is somewhat less than that of T and N and this is so for all the relationships for $b_{(\chi_2)}$ (b = coefficient in regression equation). From Equation (1) it can be seen that with an NCO/OH ratio = 1.1 the effect of the filler is more significant than that of temperature ($b_{(\chi_1)} = 5.87$; $b_{(\chi_3)} = 2.69$. For PCs obtained with NCO/OH ratios > 2 (Equations (2) and (3)) the temperature affects adhesion more than the amount of filler.

Filler introduced at various molar ratios on the basic components changes the A of the coating variously (Fig. 1). The fall in A for an NCO/OH ratio = 1.1 (Fig. 1 curve 3) is, perhaps, connected with the fact that, as a result of the interaction of the polymer with the filler and formation of polymer-filler type bonds, the number of functional groups capable of interaction with the substrate falls. Further increase in the filler concentration increases the hardness of the polyurethane film, as a result of which the recorded work A increases. The increase in A for compositions obtained with excess isocyanate component (Fig. 1, curve 1), is apparently connected with an increase in the concentration of the functional groups in unit volume. However, the excess of these groups not being unlimited, the value of the work A passes through a maximum. For a ratio 3.1 : 1 (curve 2) an increase is seen in the adhesion with increasing filler concentration but its value is less than with a PC with a two-fold excess of isocyanate groups (possibly from large internal stresses, lowering the adhesional strength of the PC).

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(Notes on completion overleaf)

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Abstract

The adhesion to steel of polyurethane coatings with titanium dioxide fillers was examined using a roller adhesiometer. It was found that adding the filler increased the hardness of the resin and its adhesion. Adhesion was also found to vary with the proportion of isocyanate to hydroxide in the resin, and increasing temperature caused a decrease in adhesion. Adhesion calculated from a mathematical model agreed with the experimental data. It was concluded that the equations obtained from the model could be used in the solution of practical problems concerned with adhesion.

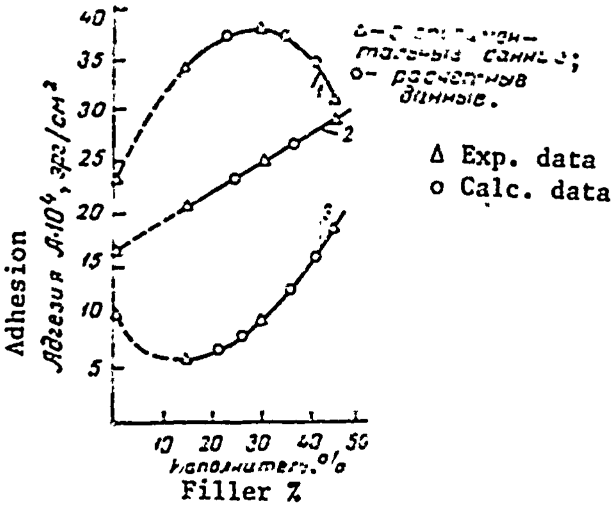

Fig. 1. Dependence of work of adhesion of polyurethane coatings on amount of filler introduced, for various ratios of NCO/OH (1-3-2.1:1; 3.1:1; 1.1:1 respectively.

Using the mathematical model, the work A was determined in various conditions, by calculation. The calculated values showed good agreement with the experimental data obtained in further experiments. Thus, from Equations (1-3) the temperature and speed depedences were calculated (Figs. 2 and 3) for the value of the work of adhesion (Fig. 4). As can be seen from Figs. 2 and 3, in every case higher temperature leads to a fall in A. This occurs because the bonds for inter-molecular interaction, which are present between the polyurethane FC and the substrate, are broken from the effect of the heat energy. Attention should be given to the fact that for a PC with a large amount of filler this fall has a more sharply expressed character than with non-filled mixes.

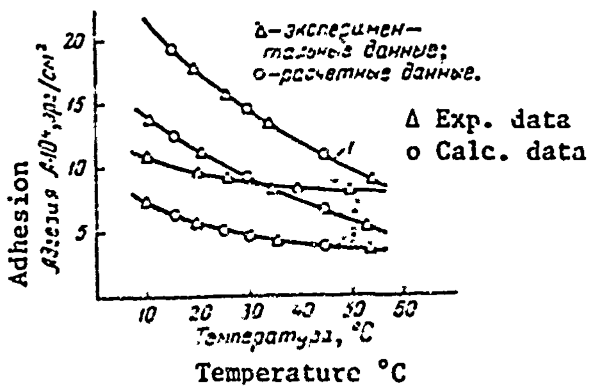

Fig. 2. Dependence of work of adhesion of filled coatings on temperature for NCO/OH:1.1/1: 1-45% TiO_2; 2-30% TiO_2; 3-15% TiO_2; 4 - without filler.

From Fig. 4 it can be seen that the calculated points agree well with the experimental ones. The dependence of the work A on the rate of shearing is seen with all the compositions, as a result of the breaking of the adhesive union being accompanied by deformation of the adhesive in the thickness direction, in the volume adjoining the zone of breakdown, and this increases the recorded value of the adhesion.

The equations obtained can be used in the solution of practical problems concerned in the determination of the conditions which give the maximum work of adhesion for the given system, given ratios of isocyanate to hydroxyl groups, concentration of filler and temperature.

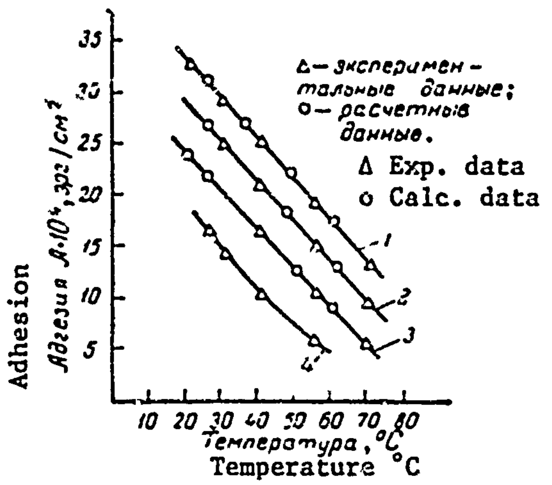

Fig. 3. Dependence of work of adhesion of filled coatings on temperature for NCO/OH = 3.1 (1-4 see Fig. 2).

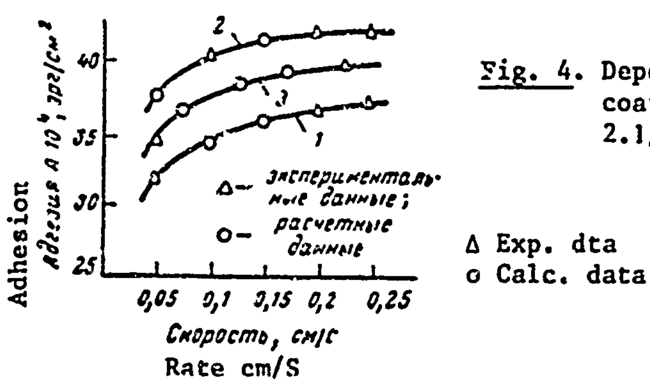

Fig. 4. Dependence of work of adhesion of filled coatings on temperature for NCO/OH = 2.1/1 (1-3 see Fig. 2)

CONCLUSIONS

1. It has been shown that the introduction of (TiO_2) filler leads to an increase in the adhesion, for an NCO/OH ratio > 2 and passes through a maximum with an NCO/OH ratio = 1.1.

2. It was shown that with increasing temperature the adhesion of polyurethane coatings falls. An increase in the rate of shearing leads to an increase in the work of adhesion, although the effect on the recorded value of adhesion is less significant compared with other factors.

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